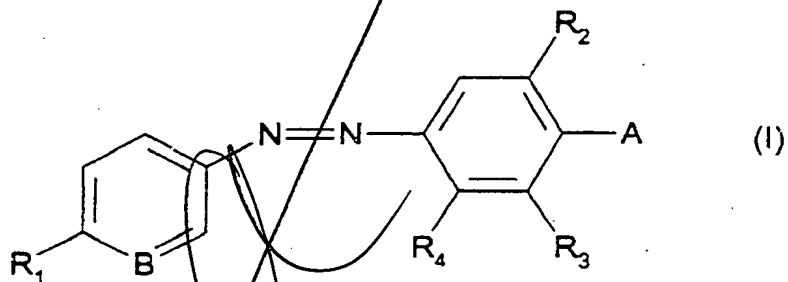


CLAIMS

1. Composition for the oxidation dyeing of keratin fibres, and in particular of human keratin fibres such as the hair, characterized in that it comprises, in a medium which is suitable for dyeing:

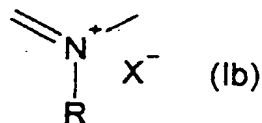
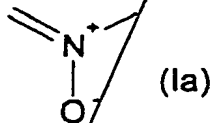
- at least one oxidation base,
- as direct dye, at least one 3-aminopyridine derivative chosen from the compounds of formula (I)

below:



in which:

- B represents a group of formula (Ia) or (Ib) below:

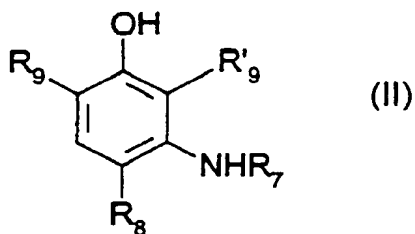


- R represents a C<sub>1</sub>-C<sub>4</sub> alkyl radical;

- R<sub>1</sub> represents a hydrogen or halogen atom such as chlorine, bromine or fluorine, or a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy radical;

- R<sub>2</sub> represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy radical;

- $R_4$  represents a hydrogen or halogen atom such as chlorine, bromine or fluorine, or a  $C_1$ - $C_4$  alkyl, nitro, amino or  $(C_1$ - $C_4)$ acylamino radical;
- $R_3$  represents a hydrogen atom or else  $R_4$  and  $R_3$  together form a 6-membered unsaturated ring bearing a hydroxyl substituent chelated with one of the nitrogen atoms of the azo double bond;
- A represents a residue  $-NR_5R_6$  in which  $R_5$  represents a hydrogen atom or a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  monohydroxyalkyl or  $C_2$ - $C_4$  polyhydroxyalkyl radical;  $R_6$  represents a hydrogen atom, a  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  monohydroxyalkyl or  $C_2$ - $C_4$  polyhydroxyalkyl radical, a phenyl ring or a  $-CH_2-SO_3Na$  radical;
- $X^-$  represents a monovalent or divalent anion and is preferably chosen from a halogen atom such as chlorine, bromine, fluorine or iodine, a hydroxide, a hydrogen sulphate or a  $(C_1$ - $C_6)$ alkyl sulphate such as, for example, a methyl sulphate or an ethyl sulphate, and
- at least one coupler chosen from the meta-aminophenol derivatives of formula (II) below, and the addition salts thereof with an acid:

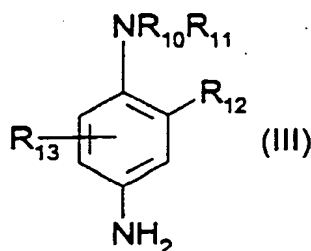


in which:

- R<sub>7</sub> represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl, C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl or C<sub>1</sub>-C<sub>4</sub> monoaminoalkyl radical;
  - R<sub>8</sub> represents a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy radical or a halogen atom chosen from chlorine, bromine and fluorine,
  - R<sub>9</sub> and R'<sub>9</sub>, which may be identical or different, represent a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl, C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkoxy or C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkoxy radical;
- it being understood that at least one of the radicals R<sub>7</sub>, R<sub>8</sub>, R<sub>9</sub> and R'<sub>9</sub> is other than a hydrogen atom.

2. Composition according to Claim 1, characterized in that the oxidation base(s) is (are) chosen from para-phenylenediamines, double bases, para-aminophenols, ortho-aminophenols and heterocyclic oxidation bases.

3. Composition according to Claim 2, characterized in that the para-phenylenediamines are chosen from the compounds of formula (III) below, and the addition salts thereof with an acid:



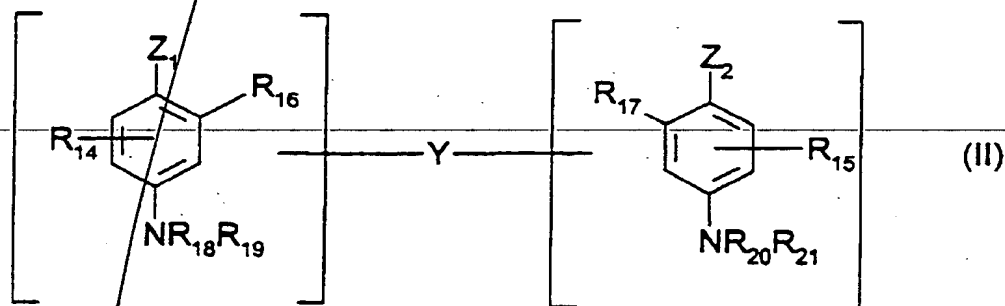
in which:

- R<sub>10</sub> represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl radical, C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl radical, (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical, C<sub>1</sub>-C<sub>4</sub> alkyl radical substituted with a  
 5 nitrogenous group, phenyl or 4'-aminophenyl;  
 - R<sub>11</sub> represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl radical, C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl radical, (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical or C<sub>1</sub>-C<sub>4</sub> alkyl radical substituted with a  
 10 nitrogenous group;  
 - R<sub>12</sub> represents a hydrogen atom, a halogen atom such as a chlorine, bromine, iodine or fluorine atom, or a C<sub>1</sub>-C<sub>4</sub> alkyl radical, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl radical, C<sub>1</sub>-C<sub>4</sub> hydroxyalkoxy radical, acetylamino(C<sub>1</sub>-C<sub>4</sub>)alkoxy, mesylamino(C<sub>1</sub>-C<sub>4</sub>)alkoxy or carbamoylamino(C<sub>1</sub>-C<sub>4</sub>)alkoxy  
 15 radical,  
 - R<sub>13</sub> represents a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl radical.

4. Composition according to Claim 3,  
 20 characterized in that the para-phenylenediamines of formula (III) are chosen from para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine,  
 25 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-β-methylaniline, N,N-bis(β-hydroxyethyl)-para-

phenylenediamine, 4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-methylaniline, 4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-chloroaniline, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-( $\beta$ -hydroxypropyl)-para-phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-( $\beta$ -hydroxyethyl)-para-phenylenediamine, N-( $\beta,\gamma$ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2- $\beta$ -acetylaminoethyloxy-para-phenylenediamine and N-( $\beta$ -methoxyethyl)-para-phenylenediamine, and the addition salts thereof with an acid.

5. Composition according to Claim 2, characterized in that the double bases are chosen from the compounds of formula (IV) below, and the addition salts thereof with an acid:



in which:

- $\text{Z}_1$  and  $\text{Z}_2$ , which may be identical or different, represent a hydroxyl or  $-\text{NH}_2$  radical which can be

substituted with a C<sub>1</sub>-C<sub>4</sub> alkyl radical or with a linker arm Y;

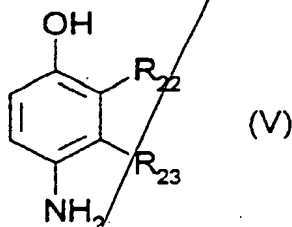
- the linker arm Y represents a linear or branched alkylene chain comprising from 1 to 14 carbon atoms, which can be interrupted or terminated with one or more nitrogenous groups and/or with one or more hetero atoms such as oxygen, sulphur or nitrogen atoms, and optionally substituted with one or more hydroxyl or C<sub>1</sub>-C<sub>6</sub> alkoxy radicals;
- R<sub>14</sub> and R<sub>15</sub> represent a hydrogen or halogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl radical, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl radical, C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl radical or C<sub>1</sub>-C<sub>4</sub> aminoalkyl radical or a linker arm Y;
- R<sub>16</sub>, R<sub>17</sub>, R<sub>18</sub>, R<sub>19</sub>, R<sub>20</sub> and R<sub>21</sub>, which may be identical or different, represent a hydrogen atom, a linker arm Y or a C<sub>1</sub>-C<sub>4</sub> alkyl radical;

it being understood that the compounds of formula (IV) comprise only one linker arm Y per molecule.

6. Composition according to Claim 5,
- characterized in that the double bases of formula (IV) are chosen from N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(β-hydroxyethyl)-N,N'-bis(4-aminophenyl)tetramethylenediamine, N,N'-bis(4-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-

methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the addition salts thereof with an acid.

7. Composition according to Claim 2, characterized in that para-aminophenols are chosen from the compounds of formula (V) below, and the addition salts thereof with an acid:



in which:

- 10 - R<sub>22</sub> represents a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl, (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl, C<sub>1</sub>-C<sub>4</sub> aminoalkyl or hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkylamino(C<sub>1</sub>-C<sub>4</sub>)alkyl radical,
- R<sub>23</sub> represents a hydrogen or halogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> monohydroxyalkyl, C<sub>2</sub>-C<sub>4</sub> polyhydroxyalkyl, C<sub>1</sub>-C<sub>4</sub> aminoalkyl, cyano(C<sub>1</sub>-C<sub>4</sub>)alkyl or (C<sub>1</sub>-C<sub>4</sub>)alkoxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical,

it being understood that at least one of the radicals

R<sub>22</sub> and R<sub>23</sub> represents a hydrogen atom.

20 8. Composition according to Claim 7, characterized in that the para-aminophenols of formula (V) are chosen from para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol,

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5           9.   Composition according to Claim 2,  
characterized in that the ortho-aminophenols are chosen  
from 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-  
methylphenol and 5-acetamido-2-aminophenol, and the  
addition salts thereof with an acid.

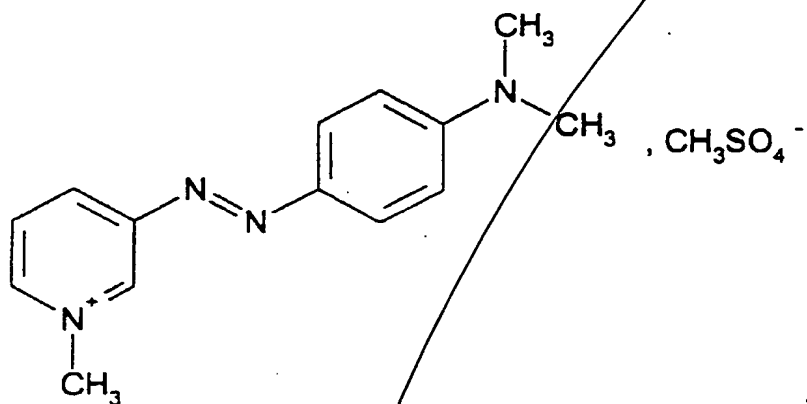
15                    11. Composition according to any one of the  
preceding claims, characterized in that the oxidation  
base(s) represent(s) from 0.0005 to 12% by weight  
relative to the total weight of the dye composition.

12 Composition according to Claim 11,  
20 characterized in that the oxidation base(s) represent(s)  
from 0.005 to 6% by weight relative to the total weight  
of the dye composition.

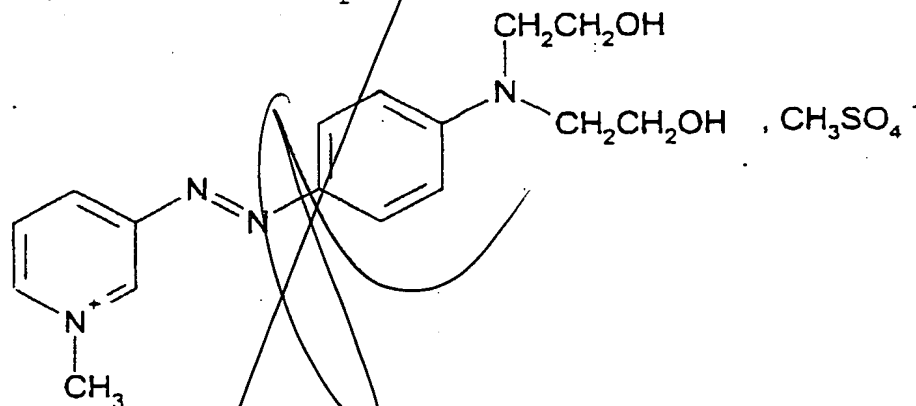
13. Composition according to any one of the preceding claims, characterized in that the 3-aminopyridine derivative(s) of formula (I) is (are) chosen from:

- 4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium  
methosulphate of formula:



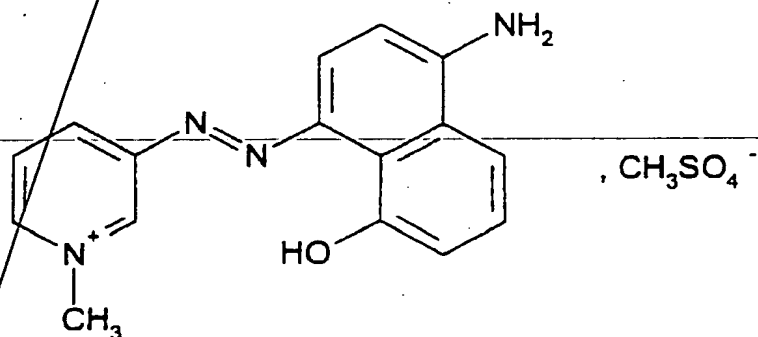


- 4'-bis(β-hydroxyethyl)aminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



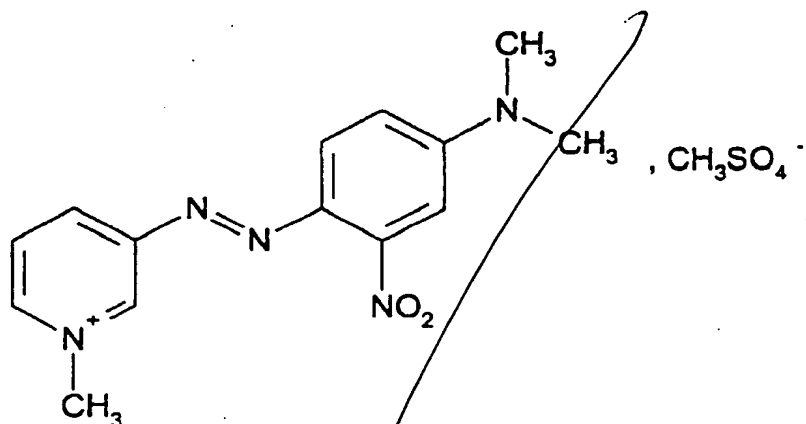
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- 4'-amino-8'-hydroxynaphthalene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

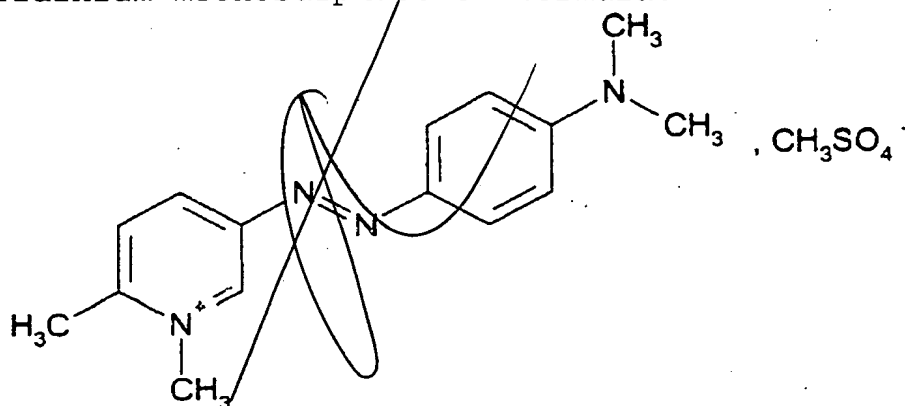


- 4'-dimethylamino-2'-nitrobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:

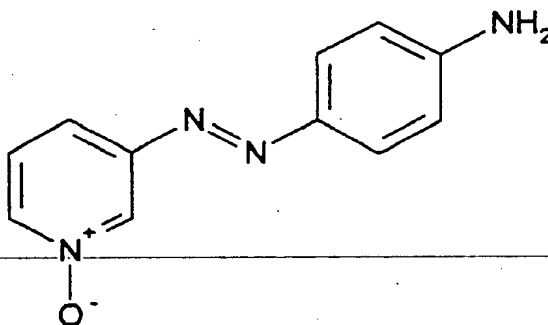
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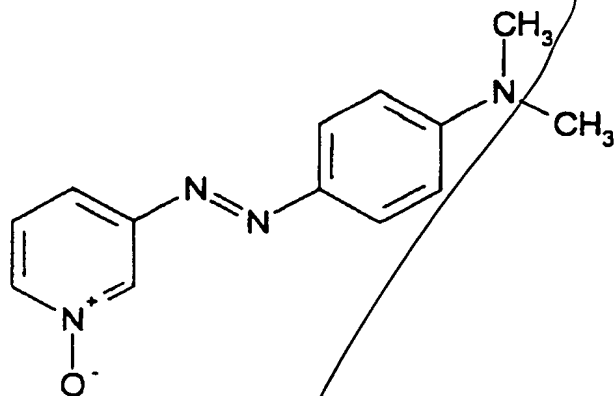
- 4'-dimethylaminobenzene-1'-azo-1,6-dimethyl-3-pyridinium methosulphate of formula:



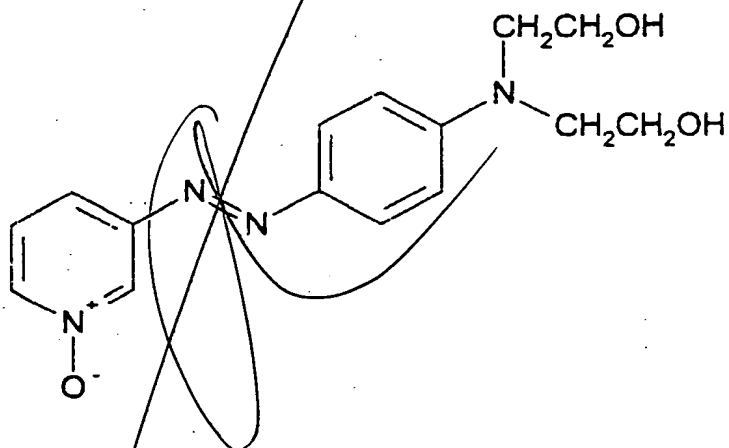
- 5 - 4'-aminobenzene-1'-azo-3-pyridine N-oxide of formula:



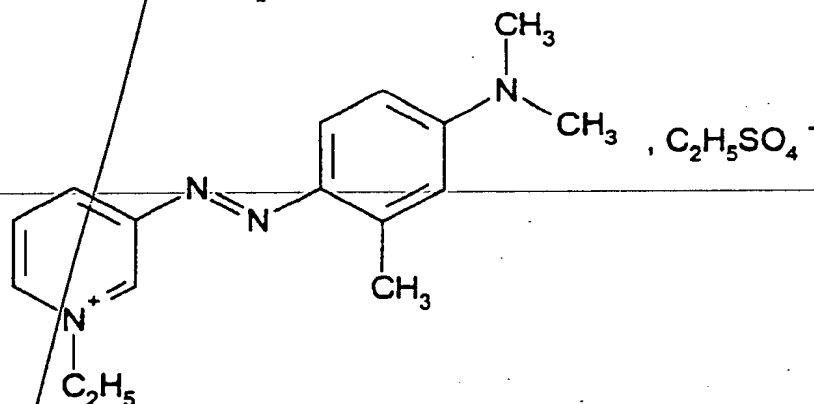
- 4'-dimethylaminobenzene-1'-azo-3-pyridine N-oxide of formula:



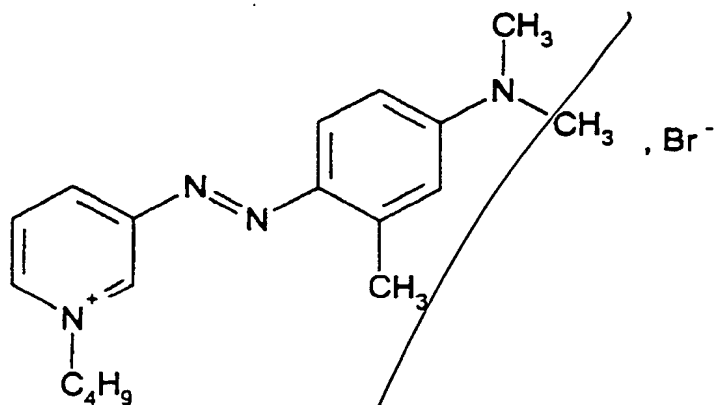
- 4'-N,N-bis( $\beta$ -hydroxyethyl)aminobenzene-1'-azo-3-pyridine N-oxide of formula:



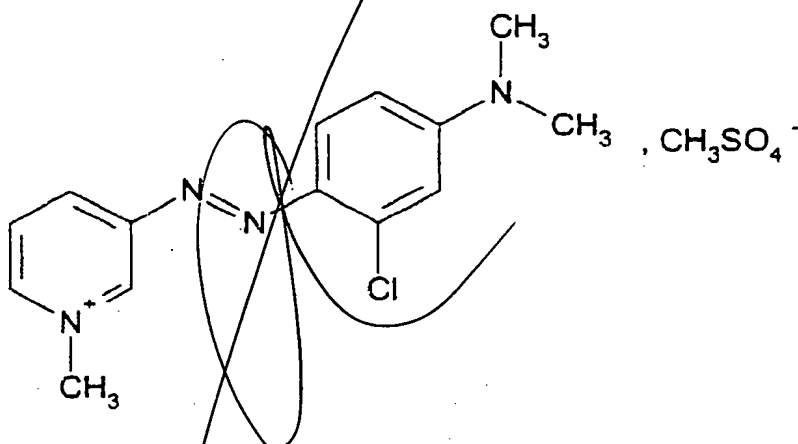
- 5 - 4'-dimethylamino-2'-methylbenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:



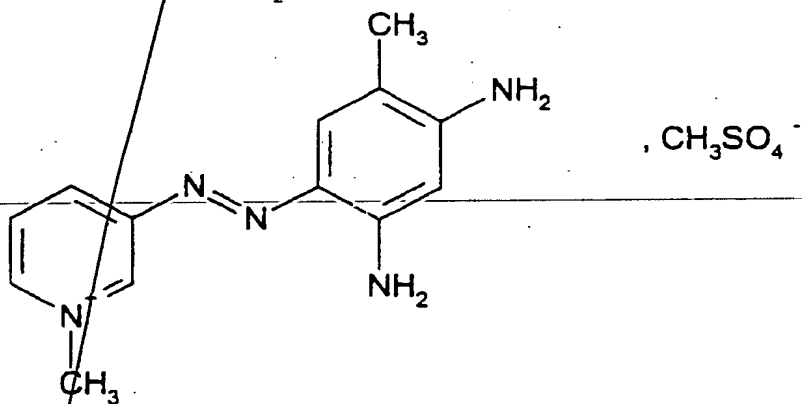
- 4'-dimethylamino-2'-methylbenzene-1'-azo-1-butyl-3-pyridinium bromide of formula:



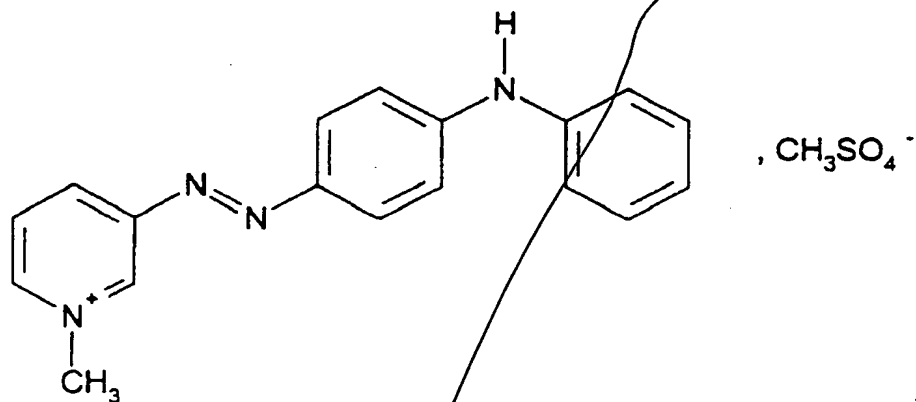
- 4'-dimethylamino-2'-chlorobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



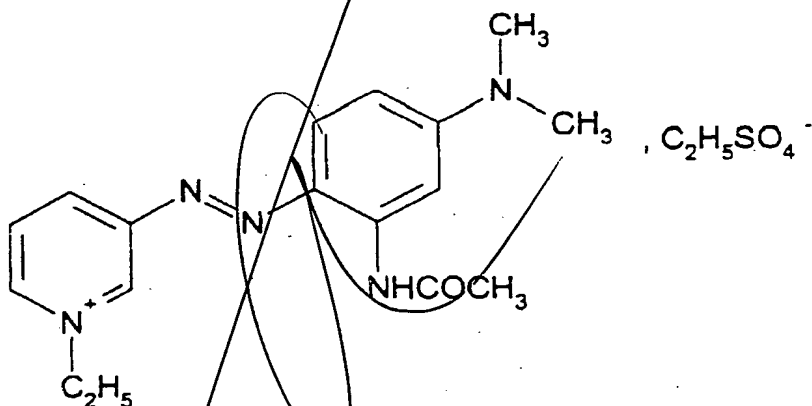
- 5 - 2',4'-diamino-5'-methylbenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



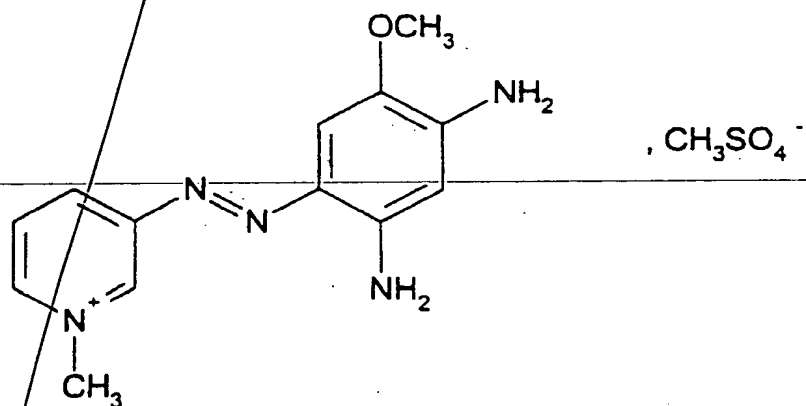
- 4'-phenylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



- 2'-acetylamino-4'-dimethylaminobenzene-1'-azo-1-ethyl-3-pyridinium ethosulphate of formula:

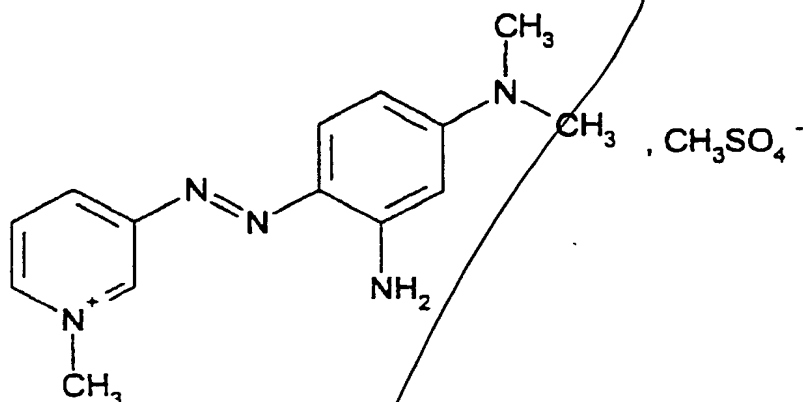


5 - 2',4'-diamino-5'-methoxybenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



and

- 2'-amino-4'-dimethylaminobenzene-1'-azo-1-methyl-3-pyridinium methosulphate of formula:



14. Composition according to any one of the preceding claims, characterized in that the 3-amino-pyridine derivative(s) of formula (I) represent(s) from 0.001 to 10% by weight relative to the total weight of the dye composition.

15. Composition according to Claim 14, characterized in that the 3-aminopyridine derivative(s) of formula (I) represent(s) from 0.01 to 5% by weight relative to the total weight of the dye composition.

16. Composition according to any one of the preceding claims, characterized in that the meta-aminophenol derivatives of formula (II) are chosen from 5-amino-2-methoxyphenol, 5-amino-2-( $\beta$ -hydroxyethyloxy)phenol, 5-amino-2-methylphenol, 5-N-( $\beta$ -hydroxyethyl)amino-2-methylphenol, 5-N-( $\beta$ -hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol, 5-( $\gamma$ -hydroxypropylamino)-2-methylphenol, 3-amino-2-chloro-6-methylphenol, 3-amino-6-chlorophenol and 3-( $\beta$ -

aminoethyl)amino-6-chlorophenol, and the addition salts thereof with an acid.

17. Composition according to any one of the preceding claims, characterized in that the meta-  
5 aminophenol derivative(s) of formula (II) represent(s) from 0.0001 to 10% by weight relative to the total weight of the dye composition.

18. Composition according to Claim 17, characterized in that the meta-aminophenol derivative(s)  
10 of formula (II) represent(s) from 0.005 to 5% by weight relative to the total weight of the dye composition.

19. Composition according to any one of the preceding claims, characterized in that it contains one or more couplers other than the meta-aminophenol  
15 derivatives of formula (II) as defined in Claim 1 and/or one or more direct dyes other than the 3-aminopyridine derivatives of formula (I) as defined in Claim 1.

20. Composition according to any one of the preceding claims, characterized in that the addition  
20 salts with an acid are chosen from the hydrochlorides, hydrobromides, sulphates, tartrates, lactates and acetates.

21. Composition according to any one of the preceding claims, characterized in that the medium which  
25 is suitable for dyeing consists of water or of a mixture of water and at least one organic solvent.

22. Composition according to any one of the preceding claims, characterized in that it has a pH of between 3 and 12.

23. Process for dyeing keratin fibres, and  
5 in particular human keratin fibres such as the hair, characterized in that at least one dye composition as defined in any one of Claims 1 to 22 is applied to the said fibres, the colour being developed at acidic, neutral or alkaline pH with the aid of an oxidizing  
10 agent which is added to the dye composition only at the time of use, or which is present in an oxidizing composition that is applied simultaneously or sequentially.

24. Process according to Claim 23,  
15 characterized in that the oxidizing agent present in the oxidizing composition is chosen from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates, percarbonates and persulphates, peracids and enzymes.

20 25. Multi-compartment dyeing device or multi-compartment dyeing "kit", a first compartment of which contains a dye composition as defined in any one of Claims 1 to 22 and a second compartment of which contains an oxidizing composition.

add  
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